CHAPTER 1

Introduction

In this chapter, we describe the basic aspects of nanoscience and nanotechnology. Further, we have presented a historical background, which led to the development of the nanoscience. Following this, properties of nanoparticles have been described with a focus on metal nanoparticles. Also, optical properties of nanoparticles have been described with special reference to surface plasmon oscillations and fluorescence from metal nanoparticles, together with various applications of the metal nanoparticles. In the last section, objectives for carrying out this research work have been put forth.
1.1 Nanoscience and nanotechnology
A nanometre (nm) is one billionth of a metre, i.e., \(10^{-9}\) m, this is roughly 10 times the size of an atom, while a human hair is approximately 80,000 nm wide. Within this length scale, properties of matter are significantly different from individual atoms or molecules and from bulk material as well. At this length scale, it is possible to vary the fundamental properties of materials, i.e., melting temperature, mechanical strength, magnetization, charge capacity, burning rate, optical properties, catalytic and sensing capabilities to name a few. The study and manipulation of materials at nm length scale, where properties differ significantly from atom as well as from bulk is recognized as a new branch of science, better known as nanoscience. Nanoscale materials have high surface area to volume ratio, making them ideal for use in composite materials, drug delivery, catalysis, sensors, data storage and energy storage. Finite size of material entities as compared to the molecular scale makes nanostructured materials harder, less brittle and mechanically strong. On the other hand, nanotechnology is the creation of functional materials, devices and systems through control of matter on nm (1 to 100 nm) length scale and exploitation of the novel properties and phenomena developed at this length scale. Nanoscience and nanotechnology [1-4] is truly interdisciplinary, with an understanding of physics and chemistry of the matter and the processes at nanoscale, we can look for their applications in biology or medicine and vice-versa.

1.2 Why is length scale so important?
Nanomaterials have properties different from those of atoms and bulk materials. This difference in properties of the nanomaterials is due to their high surface area to volume ratio, and dominance of quantum size effect. An increase in surface area to volume ratio will result in more atoms on the surface and hence, result in a corresponding increase in chemical reactivity, making some nanomaterials useful as catalysts, as sensors, in data storage, and to improve the efficiency of fuel cells [5-8]. As the size of matter is reduced to 10’s of nm or less, quantum size effects [9, 10] can begin to play a role, and these can significantly change a material’s optical, magnetic or electrical properties. Size dependent properties have been exploited for centuries. For example, gold and silver nanoparticles
(particles of diameter less than 100 nm) have been used as coloured pigments in stained glasses and ceramics since 4th century [11]. Depending on their size, gold particles can appear red, blue or gold in colour. All properties of the nanomaterials, different from their bulk and atom counterparts, are due to their size.

1.3 Classification of nanomaterials

Nanomaterials have significantly different properties than other materials due to their length scale. Although, a broad definition, we categorize nanomaterials as those which have structured components with at least one dimension less than 100 nm. When, none of the three dimensions of a particle is in nm length scale, it is known as a bulk material (Figure 1.1a). If only one dimension of a particle is in nm, structure is known as a Quantum Well (Figure 1.1b), and electronic structure is quite different from, where two dimensions are in nm, constituting what is known as a Quantum Wire (Figure 1.1c). A Quantum Dot/ Nanoparticle (Figure 1.1d) has all three dimensions in nm length scale [1-3].

**Figure 1.1.** Schematic representation of (a) bulk (b) Quantum Well (c) Quantum Wire (d) Quantum Dot/ Nanoparticle.

**Density of states:** Another important factor responsible for the interesting properties of the low dimensional systems is density of states (DOS) [1-3]. The density of state (D
(E)) is defined as the number of energy levels \{N(E)\} in a given energy interval \{dE\}. Mathematically \(D(E)\) is defined as:

\[
D(E) = \frac{dN(E)}{dE}
\]

When a particle having bulk like properties is reduced in size to a few hundred of atoms, density of states in the valence band, the topmost band containing electrons, changes dramatically. The continuous density of states in the band is replaced by a set of discrete energy levels (Figure 1.2). It was revealed that many of the differences between electronic behaviour of the bulk and the quantum confined low dimensional systems (nanomaterials) are due to the difference in their density of state.

**Bulk**: In a system, when none of the three dimensions (3d) is in nm. The DOS has the form

\[
D(E) = \left(\frac{m}{\hbar^2}\right)^{3/2} \frac{V}{\pi^2} E^{1/2}
\]

Where \(V\) is crystal volume and \(m\) is electron mass. Thus, DOS for bulk materials is a square-root function of energy (Figure 1.2a).

![Figure 1.2. Schematic representation of density of states for (a) bulk, and Q-Well (b) Q-Wire (c) Q-Dot/ Nanoparticle.](image-url)
**Q-Well**: When one dimension of a particle is in nm and rest two (2d) are bulk like (Q-Well), energy levels are discrete along one direction due to quantum confinement effects. Hence, DOS for a Q-Well has the form

\[ D(E) = \frac{S m}{\pi \hbar^2} \sum_n \Theta(E - E_n) \]

Where \( S \) is area of surface of the Quantum well and \( \Theta(x) \) is Heaviside step function, i.e.,

\[ \begin{cases} \Theta(x) = 1 & \text{for } x > 0 \\ \Theta(x) = 0 & \text{for } x < 0 \end{cases} \]

Each term in the sum corresponds to the contribution from one subband. The contributions of all subbands are equal and independent of energy. As a result, DOS for a Q-Well exhibits a staircase shaped energy dependence, with each step being associated with one of the energy states \( E_n \), is constant of energy and behaves like a step function (Figure 1.2a).

**Q-Wire**: When two dimensions of a particle are in nm and one (1d) is bulk like, i.e., Q-Wire, energy levels are discrete along two directions and DOS for a Q-Wire has the form

\[ D(E) = \frac{L_x}{\pi} \left( \frac{2m}{\hbar^2} \right)^{\\frac{3}{2}} \left( \frac{1}{E - E_{n_{\perp} n_2}} \right)^{\\frac{3}{2}} \Theta(E - E_{n_{\perp} n_2}) \]

Where \( L_x \) is length of the Q-wire and \( \Theta(x) \) is Heaviside step function. Instead of step function behaviour of the Q-well, DOS for a Q-wire diverges at the bottom of each subband and then decreases as the kinetic energy increases. This shows that DOS of a Q-Wire has a square root singularity (Figure 1.2b).

**Q-Dot/ Nanoparticle**: When all the three dimensions of a particle are in nm (0d), i.e., Q-Dot, energy states of an electron get confined along all the three directions due to quantum confinement effect.

The DOS of a Q-Dot/ Nanoparticle has the form
\[ D(E) = \sum_{v} \delta(E - E_v) \]

where \( E_v \) is energy associated with the quantum state \( v \), i.e., \( v = (n_1, n_2, n_3) \). Therefore, energy dependence of DOS for a Q-Dot/ Nanoparticle [1-3] is a \( \delta \)-function (Figure 1.2c).

### 1.4 Historical background

The existence of functional devices and structures at nm dimensions is not new, and in fact such structures have existed on earth as long as life itself. The natural world contains many examples of nanoscale structures, from milk (a nanoscale colloid) to nanostructured proteins that control a range of biological activities. Nanoparticles occur naturally, and have been created for thousands of years as the product of combustion and food cooking. It is not clear, when humans first began to take advantage of nanosized materials. It is known that in the 4\textsuperscript{th} century A.D. Roman glassmakers were fabricating glasses containing nanosized metals.

![Figure 1.3](image)

**Figure 1.3.** Lycurgus cup (a) in reflected light (b) in transmitted light (c) stained glass window of a medieval cathedral.

An artifact from this period called the Lycurgus cup (Figure 1.3a and b) resides in the British museum in London [12]. The cup, which depicts the death of King Lycurgus, is
made from soda lime glass containing gold nanoparticles. The colour of the cup appears
green in reflected light and red in transmitted light. Also, great varieties of beautiful
colours of the windows of medieval cathedrals (Figure 1.3c) are due to the presence of
metal nanoparticles in the glass. Further, photography developed in the 18-19th centuries,
also, depend upon the production of silver nanoparticles sensitive to light [1-3].
Photographic film is nothing but an emulsion (a thin layer of gelatine containing silver
halides, such as silver bromide, and a base of cellulose acetate). Light decomposes the
silver halides, producing nanoparticles of silver, which are the pixels of images. In India
people have been using Kajal to protect the eyes from ailment since thousands of years.
This Kajal is prepared by mixing the soot of an oil lamp (carbon nanoparticles) with
clarified butter. Optical properties of Au nanoparticles indeed filled Michael Faraday
with enthusiasm, when he reported in 1857 the synthesis of colloidal solutions of Au
nanoparticles exhibiting colours ranging from ruby red to amethyst [13].

Various approaches for describing the interaction between light and nanostructures were
reported in the beginning of the 20th century. Maxwell-Garnett developed a model [14],
the so called effective medium theory, which gives the expression of the dielectric
constant of metal spheres dispersed in a medium of dielectric constant $\varepsilon_m$, provided size
of the sphere is small compared to the wavelength of light and the material under
consideration have spatial extension larger than the wavelength of light. Another theory
was given by Debye, where he envisaged the impact of light on nanoparticles as if light is
exerting a mechanical pressure on it [14]. However, the most successful theory, without
contest, is the one given by Gustav Mie [15] in 1908 to provide an explanation of the
dependence of the colour of glasses on metal size and kind. Here, the problem was
treated as a scattering one and Maxwell’s equations were used for spherical particles
(dielectric constant $\varepsilon$) embedded in a medium (dielectric constant $\varepsilon_m$). Mie presented a
solution to Maxwell’s equations that describe the extinction spectra of spherical particles
of arbitrary size.

Richard Feynman [4] presented a visionary and prophetic lecture (1959) at a meeting of
the American Physical Society, entitled “There is Plenty of Room at the Bottom,” where
he speculated on the possibility and potential of nanosized materials. One of the most
ambitious statements in that talk was, “The principles of physics, as far as I can see, do
not speak against the possibility of manoeuvring things atom by atom. It is not an attempt to violate any laws; it is something, in principle, that can be done; but in practice, it has not been done because we are too big”. Feynman explored the possibilities of manipulating material at the scale of individual atoms and molecules, imagining the whole of the Encyclopaedia Britannica written on the head of a pin and foreseeing the increasing ability to examine and control matter at the nanoscale.

The term ‘nanotechnology’ was not used until Norio Taniguchi (1974), a researcher at the University of Tokyo in Japan, used it to refer to the ability to engineer materials precisely at the nm level [1-3]. The primary driving force for miniaturisation at that time came from the electronic industry, which aimed to develop tools to create smaller, faster and more complex electronic devices on silicon chips. A technique called electron beam lithography [1] was used to create nanostructures and devices as small as 40–70 nm in the early 1970s. The size range that holds so much interest is typically from 100 nm down to the atomic level (approximately 0.2 nm), because it is in this range (particularly at the lower end) that materials can have different or enhanced properties compared with the same material in bulk.

The impetus to nanoscience and nanotechnology is also given by a renewed interest in colloidal science, coupled with a new generation of analytical tools, such as, atomic force microscope (AFM), scanning tunnelling microscope (STM), scanning electron microscope (SEM), transmission electron microscope (TEM) [16-19], which enable surface and interfacial characterization of materials at the nm length scale. Further, AFM and STM allow individual atoms to be observed, analysed and manipulated. This has guided to greater understanding of the relationship between form and material properties, and enabling the control of processes at nm length scale and designing materials with specific properties.

### 1.5 Metal nanoparticles

In nanoscience, the study of metal nanoparticles [5, 20-25] has been a source of immense interest due to their novel properties different from those of metal atoms and bulk metal. This makes them candidates with significant potential in a wide range of applications, such as, in catalysis, magnetic recording, optoelectronics, magnetic fluids, composite
materials, fuel cells, pigments, MRI contrast agent, bio-labeling and sensors [6-8, 26-28]. Uniqueness in properties of metal nanoparticles arises due to their high surface area to volume ratio and quantum size effect, resulting from their reduced size. First, let us discuss the surface area to volume ratio and the quantum size effect for metal nanoparticles.

1.5.1 Surface area to volume ratio

Uniqueness in properties of nanoparticles arises due to their high surface area to volume ratio, resulting from their reduced size. As size of a particle decreases, a greater proportion of atoms are found at the surface compared to those inside. For example, a particle of size 30 nm has 5% of its atoms on its surface, at 10 nm this is 20%, and at 3 nm 50% of the atoms are on its surface. Thus, with decrease in size of a nanoparticle, number of atoms on the surface increases proportionally, i.e., surface area to volume ratio increases as size of the nanoparticle decreases. Sensor and catalytic properties depends upon the number of atoms on the surface and hence nanomaterials act as a good sensor and catalyst.

1.5.2 Quantum size effect

When atoms combine to form a bulk material, the discrete energy levels of atoms are smudged out into energy bands. When a metal particle having bulk like properties is reduced in size to a few hundred of atoms, a reversal takes place, and the density of states in the valence band, the topmost band containing electrons, changes dramatically. The continuous density of states in the band is replaced by a set of discrete energy levels. In this situation, the energy levels can be treated quantum mechanically, which is referred to as the quantum size effect [9, 10]. Quantum effects arise in systems which confine electrons to regions comparable to their de Broglie wavelength. Due to quantum confinement effect, there is change in the optical properties of nanoparticles as a function of size, observed as a blue shift in absorption spectrum and development of discrete features in the spectrum. Quantum effects not only cause the increase in the energy gap (blue shift of the absorption edge) and the splitting of the electronic states, but also changes the densities of states. The emergence of new properties can be understood in
terms of the Heisenberg Uncertainty Principle, which states that more an electron is
spatially confined the broader will be its range of momentum. And the average energy
will not be determined by the chemical nature of the atoms, but mainly by the dimension
of the particle. And hence, the small metal cluster is analogous to a mesoscopic atom
having discrete energy levels.

1.6 Optical properties of metal nanoparticles
A nanoparticle can be thought of as a system of bound atoms. As a broad classification,
we can think of two schemes [29] characterizing the process of interaction of light with
metal nanoparticles. In the first scheme, the optical properties of the metal nanoparticles
are dominated by collective oscillations of the conduction electrons in the
electromagnetic field of light. These properties are mainly observed in Ag, Au and Cu
nanoparticles because of availability of the free conduction electrons and a strong
absorption band is observed in the visible region. In the second scheme, the main part of
interaction takes place between the outer conduction electrons and their atomic cores,
whereby radiative transitions are similar to those occurring in solitary atoms, so that
absorption spectrum consists of individual lines or bands in the absorption spectrum of
metal nanoparticles. However, for the majority of metal nanoparticles in the size range
<10 nm, there is only a continuous absorption in the visible range, rising to broad and
poorly resolved bands in the ultra-violet region. Thus, for these cases, the metal
nanoparticles suspensions are dull or grayish in colour.

1.6.1 Surface plasmon
When light interacts with metal nanoparticles, an absorption band is observed in the
visible range due to collective oscillations of the conduction electrons of the metal
nanoparticles. This collective oscillation of the surface electrons in the electromagnetic
field of light, which give rise to absorption band in the visible range for the metal
nanoparticles, is known as surface plasmon [30-32]. This is schematically depicted in
Figure 1.4, where the oscillating electric field of light causes the conduction electrons to
oscillate coherently. Here, the displacement of the conduction electron charge cloud relative to the nuclei in the electromagnetic field of the light is shown schematically.

Figure 1.4. Schematic representation of the surface plasmons for a metal sphere.

Gustav Mie [15] was the first to give an explanation of the dependence of the colour of metal nanoparticles on their size and type. He treated the problem as a scattering one and Maxwell’s equations were used to find the solution. Mie presented a solution to Maxwell’s equations that describe the extinction spectra (Extinction = scattering + absorption) of spherical particles of arbitrary size. Extinction cross-section of a spherical particle with radius R, and a frequency dependent complex dielectric constant, i.e., \( \varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2 \), embedded in a medium of dielectric constant \( \varepsilon_m \) and interacting with light of wavelength \( \lambda \) is given by:

\[
C_{\text{ext}} = \frac{24\pi^2 R^3 \varepsilon_m^{3/2} \varepsilon_1}{\lambda(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2^2} \]  

So, an absorption peak occurs when \( \varepsilon_1 = -2\varepsilon_m \). Further, dielectric constant \( \varepsilon(\omega) \) is given by Drude theory of free electrons.

\[
\varepsilon(\omega) = \varepsilon_m - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma} \]
Where, $\omega_p$ is plasmon frequency and $\Gamma$ is damping constant. Considering $\varepsilon_\infty = 1$ and $\Gamma \ll \omega$.

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} - \frac{1}{\pi \omega}$$

Where $\omega_p$ is the plasmon frequency and $\varepsilon$ is the dielectric function. 

$$\omega_p^2 = \frac{4\pi ne^2}{m_e}$$

Where $e$ and $m_e$ is charge and mass of an electron and $n$ is electron density. The position, shape and intensity of the surface plasmon peak strongly depend on various factors: the dielectric constant of the surrounding medium, shape and size distribution of the metal nanoparticles.

### 1.6.2 Fluorescence properties

The special properties of metal nanoparticles are primarily due to their size. The upper limit on the size of metal nanoparticles that shows interesting properties, different from those of the bulk, is at most 20 nm. Furthermore, physicists and chemists have been interested in the electronic structure of metal nanoparticles because of the quantum size effect, which has been shown to appear in metal nanoparticles having size approximately in the range of 1-10 nm. Consequently, as the size of a material is reduced down to nanoscale dimension and further, its electronic properties change drastically, whereby the electronic structure of the material changes from continuous energy bands of the bulk state to discrete energy levels of atoms, shown in Figure 1.5 [1, 9 & 10]. The colour of light emitted by a material is determined by the radiative transitions taking place. When light is incident on the metal nanoparticles, absorption of light can occurs due to transitions of outer electrons to higher energy levels. Nanoparticles of different sizes will have different energy level separations as shown in Figure 1.5. A fraction of the absorbed light by the nanoparticles may be re-emitted as light of longer wavelength in the visible and near-visible region of the spectrum. This phenomenon of photons emission following absorption of photons by nanoparticles is known as fluorescence [33].
Figure 1.5. Schematic representation of changes in the energy levels occurring from (a) bulk (b) to a large metal nanoparticle and then (c) to a small metal nanoparticle.

Figure 1.6 shows the schematic of absorption and fluorescence processes. Electrons in the ground state absorb light to make transition to some excited states such that $E_0 + h\nu_1 = E_1$ or $E_0 + h\nu_2 = E_2$ and the process is known as absorption. The excited electrons, after relaxation de-excites back to the ground state.

Figure 1.6. Schematic of absorption and fluorescence processes.
Excited electrons while de-exciting emit a photon of light such that $E_1 = E_0 + h\nu$ and the process is known as fluorescence [33, 34]. There are other processes (vibrational relaxation, internal conversion) accompanying the fluorescence emission, which have also been schematically shown in Figure 1.6. Light induced transitions between these levels determine the colour of the light emitted by a material. This signifies that nanoparticles of different sizes can emit light of different colours, and the size of the nanoparticles can be used to engineer the colour of the light emitted. These colours are not only absent for the bulk material, but also for the atoms. The most notable colours are found in dispersions of gold, silver and copper nanoparticles.

![Figure 1.7. Metal nanoparticles dispersed in water and kept in natural light (left), and UV-light (right).](image)

Thus, the fundamental problem of how molecular electronic properties evolve with increasing size in this transitional region between molecular and solid-state physics continues to be addressed. Figure 1.7 shows the metal nanoparticles dispersed in water, kept in natural light (left), and kept in UV light (right). Under UV light, the metal nanoparticles, dispersed in water, emit beautiful colours: (a) Nano-Cu; green (b) Nano-Ag; blue (c) Nano-Al; light cyan (d) Nano-Fe; green.
1.7 Nanostructures preparation

Molecular beam epitaxy (MBE) and lithography developed in 1960s [1, 35, 36] are the two well established techniques, where nanostructures with precision can be made. In solid-source MBE, ultra-pure elements are heated until they begin to slowly evaporate. The evaporated elements then condense on the substrate (wafer), where they may react with each other. The term beam simply means that evaporated atoms do not interact with each other or vacuum chamber gases until they reach the substrate, due to the long mean free paths of the beam. In MBE, a slow deposition rate (1 to 300 nm per minute) allows the films to grow epitaxially (one atom layer after another). Intricate structures of layers of different materials may be fabricated this way. Precise control in MBE has allowed the development of nanostructures where the electrons can be confined in space. Such layers are now a critical part of many modern semiconductor devices, including semiconductor lasers and light-emitting diodes.

In lithography, nanostructures are made by a processing sequence which begins with a computer generated mask with nanostructures pattern defined by transparent and opaque regions. A thin layer of a photoresist is then deposited onto the sample (wafer). After exposing the photoresist with a light source (generally UV-light) flashed through the mask onto the sample. The mask image is transferred onto the photoresist following chemical development. The nanopatterned photoresist, in turns, acts as a resistant for the underlying material. The material from the other region (where no photoresist is present) is processed with chemical treatment, ion implantation or other appropriate processes. Finally, the photoresist is stripped, leaving the sample with nanostructures pattern.

Although, the MBE and lithography are well established modern techniques to prepare the nanostructures, but even in the 4th century A. D. Roman glassmakers were fabricating glasses containing nm size metal particles. Various chemical, biological and physical methods [37-40] have been developed or in the process of development for metal nanoparticle synthesis. Metal nanoparticles can be prepared in two distinct ways, i.e., by division of bulk metals into nanoparticles (like in lithographic technique) known as top-down approach or by growth of nanoparticles starting from metal atoms (like in MBE) known as bottom-up approach. We have developed a novel, physical, top-down process.
of electro-exploding wire (EEW) [41-44] in our laboratory to synthesize the metal nanoparticles.

1.8 Why metal nanoparticles?

Metal nanoparticles have been a source of immense interest due to their novel properties, different from those of metal atoms and bulk metal. They have remarkable optical, electronic, catalytic and magnetic properties due to their high aspect ratio and quantum confinement effect. This makes them candidates with significant potential in a wide range of applications, such as, in catalysis, magnetic recording, optoelectronics, magnetic fluids, composite materials, fuel cells, pigments, MRI (magnetic resonance imaging) contrast agents, bio-labels, sensors, as fuel in rocket propellant, in environment remediation, and in hemoglobinopathy. Here, we will discuss in brief some applications of metal nanoparticles in various fields.

**Catalysis:** Catalysis is the process of accelerating/decelerating the rate of a chemical reaction by addition of a substance known as catalyst, which is not consumed during the reaction. Metal nanoparticles can act as better catalyst [45] for industrial application as they have large surface area to volume ratio. Which means, increase in reactivity of the catalyst and therefore metal nanoparticles are promising materials for catalysis. For example, carbon nanotube composite materials were produced by catalytic decomposition of gaseous carbon sources (such as carbon monoxide or hydrocarbons) on nm-size metal clusters of iron, cobalt and nickel embedded in matrices of inert metal oxide particles. The resulting multiwalled carbon nanotubes are several micrometers long with tube diameters ranging from 5 to 20 nm.

**MRI contrast agents:** MRI uses a magnetic field, contrast agent and pulses of radio wave energy to produce pictures of organs and structures inside the body. In many cases, MRI gives information that cannot be seen with an X-ray, ultrasound, or computed tomography scan. For doing a MRI, the area of the body being studied is placed inside a special machine that is a strong magnet. In some cases, a contrast material is used during the MRI to show pictures of organs or structures more clearly. Superparamagnetic metal
nanoparticles (e.g., Fe nanoparticles) are proving as a better class of contrast agents for MRI [46].

**Environment remediation:** Inorganic contamination of water is a significant environmental hazard for drinking water. In aqueous environments, Fe acts as the electron donor and reduces the contaminants. Usually, the contaminants are transformed into less toxic or even benign products. Recently, Fe nanoparticles have been used for remediation of water, where nanoparticles reduce chlorinated hydrocarbons, hexavalent chromium, and perchlorate, most common contaminants present in water. Reaction rates reported for Fe nanoparticles are typically 2-3 times greater than reaction rates reported for granular irons (diameter approximately 1-2 mm). This disparity may be the result of size-mediated changes in surface reactivity, i.e., the high surface area to volume ratio in case of the Fe nanostructures. Similarly, other metal nanoparticles can be explored for environment remediation applications [47-49].

**Magnetic recording media:** Thin films of the magnetic nanoparticles are very good candidates for high density recording media with low noise characteristics, where each particle is more or less magnetically isolated by a non-magnetic matrix, particularly by an amorphous phase. Many of these materials exhibit perpendicular magnetic anisotropy and consequently can be used as perpendicular recording media [50-52].

**Bio-labeling and sensor:** Multi-colour labeling of both fixed and living cells with fluorescent metal nanoparticles conjugated with biological ligands that specifically bind against certain cellular targets, and enables the recording of diffusion pathways in receptor cells. Uptake of nanoparticles into the vesicular compartments around the nucleus of cells can be used to label the cells so that their pathway and fate can be followed. Nanoparticles exhibit reduced photobleaching as compared to traditional dyes and are passed on to daughter cells during cell division, therefore allowing for much longer observation. Magnetic nanoparticles can also act as sensors for assessing how external stress affects changes in intracellular biochemistry and gene expression. Colloidal metal nanoparticles have been found to strongly enhance the native signals of
chemical constituents in cells. Surface Enhanced Raman Spectroscopy relies on this signal magnification and serves as a tool for ultra-sensitive monitoring of the intracellular distribution of chemicals [7, 8 & 53].

**Optical data storage:** Metal nanoparticles produce strong visible fluorescence and exhibit emission wavelength dependence on particle size and geometry. This property of strong visible fluorescence of the metal nanoparticles can be employed for high density optical data storage. Peyer et al. [5] have shown the successive image/data writing on nanoscale silver oxide thin films (showing photoactivated visible fluorescence) using the blue excitation. The stored data can be read by blue or green light, even up to many hours after being written, without substantial degradation.

**Fuel in rocket propellant and explosive:** It is now well known that fine Al powders can form explosive mixture with air. Indeed, it is the highly exothermic reaction of Al powders with oxygen that confers the desirable reducing and propulsive properties to the powder. As the size of the powder decreases to nm range, the explosive ability of the Al powder increases. Most of the applications for the nano-Al powder are aimed to exploit the vast quantities of energy stored in. Fuels for space, naval vehicles and propellants for the space industry are the areas for the applications of nano-Al powders [54, 55].

**Water purification:** Clean water (water that is free of toxic chemicals and pathogens) is essential for life on Earth. Advances in nanoscale science and engineering are providing unprecedented opportunities to develop more cost effective and environmentally acceptable water purification processes. Fe nanoparticles and bimetallic (Fe/Pd, Fe/Pt) nanoparticles have emerged as effective redox media for the detoxification of organic and inorganic pollutants in aqueous solutions. These nanomaterials (10–100 nm) have larger surface area and reactivity than bulk Fe particles. These nanoparticles can reduce a variety of organic pollutants (e.g., chlorinated alkanes and alkenes, chlorinated benzenes, pesticides, organic dyes, nitro aromatics, PCBs) and inorganic anions (e.g., nitrates) in aqueous solutions to less toxic and recalcitrant by-products. Fe and bimetallic Fe nanoparticles have also been successfully used to reduce active metal ions such as Cr(VI)
to less toxic and mobile Cr(III) species. Ag nanoparticles are effective biocides against Escherichia coli. Cellulose acetate (CA) fibers with embedded Ag nanoparticles are also effective biocides against Gram-positive and Gram-negative bacteria including Staphylococcus aureus, Escherichia coli, Klebsiella pneumoniae and Pseudomonas aeruginosa. The integration of the nanomaterials into existing water purification systems is another key challenge. The environmental fate and toxicity of nanomaterials are also critical issues in materials selection and design for water purification. Not much is, however, known about the environmental fate, transport and toxicity of the nanomaterials [56, 57].

In hemoglobinopathy: Human blood has different variants of hemoglobin. Non-thalassemic person blood hemoglobin has HbA0 as the major component and thalassemic person blood hemoglobin can have HbA2, HbE variants too. When the interaction of Cu nanoparticles with different variants of human hemoglobin is studied, it is found that Cu nanoparticles interact differently with different variants of the human hemoglobin, i.e., with HbA0 (the major component of human hemoglobin) and HbA2 (a variant that is associated with beta thalassemia). In case of interaction with HbA0, Cu nanoparticles triggers protein aggregation and this is followed by the precipitation of the protein. While, in case of interaction of Cu nanoparticles with HbA2, no aggregation is observed. This differential interaction of the Cu nanoparticles with different variants of haemoglobin has been verified by using atomic absorption spectroscopy, high pressure liquid chromatography, dynamic light scattering, and Zeta potential measurements. From this differential interaction of the Cu nanoparticles with different variants of hemoglobin, a thalassemic person can be easily distinguished from a non-thalassemic [58].

1.9 Thesis objectives

In recent years, nanoscience has become one of the most important and exciting field of research. It shows great promises for coming years with many breakthroughs that will change the direction of technological advancement and will have wide range of applications. Metal nanoparticles have been a source of immense interest due to their
novel physical and chemical properties, different from those of metal atoms and bulk metal. They have remarkable optical, electronic, catalytic and magnetic properties due to their high surface area to volume ratio and quantum confinement effect. This makes them candidates with significant potential in a wide range of applications as explained in previous section. As a result, scientists working in the field of nanoscience and nanotechnology are using different approaches to synthesize metal nanoparticles, such as, gas evaporation, arc plasma, sputtering, chemical reaction, electrochemical method, laser ablation, reverse micelles, reduction methods etc., which have been described in detail in chapter 2. There are various issues which have to be discussed for the metal nanoparticles research, which are as follows:

(1) Very important requirement in synthesis of metal nanoparticles is their purity. The synthesized metal nanoparticles should be pure with no contamination of any kind. Contamination will affect the properties of the metal nanoparticles. In most of the synthesis process for metal nanoparticles, chemicals are used at one stage or the other. So, the purity of the nanoparticles is always questionable.

(2) The nanoparticles should be bare so that they can be easily tagged (with a required proteins, polymers, ligands etc.) and can be easily dispersed in a medium of choice (polar/ nonpolar) for further characterization and applications. This is possible if and only if synthesized metal nanoparticles are bare. When chemicals are involved in synthesis of the metal nanoparticles, then metal nanoparticles remains coated with the chemicals.

(3) High rate and low cost of production of the metal nanoparticles by a technique is most desirable thing in the field of nanoscience and nanotechnology.

(4) Study of optical (UV-visible and fluorescence) properties of the metal nanoparticles gives the impetus for their use in bio-labeling, optical data storage and as a sensor besides giving information about the band structure of the metal nanoparticles. Recently, there have been few reports in the literature on the study of fluorescence properties of Ag nanoparticles [5, 21]. But, hardly, any report on the fluorescence properties of the other
metal nanoparticles of Cu, Al and Fe. A study of fluorescence properties in detail of the metal nanoparticles of Ag, Cu, Fe, and Al is essential not only from application point of view but also to know the electronic levels operating in the metal nanoparticles.

We take into account all the above issues in the present research of metal nanoparticles. **Chapter 2** describe the synthesis of pure metal nanoparticles of Cu, Fe, Ag, and Al by employing a novel, physical, top-down, semi-continuous process of EEW that we have established in our laboratory. In the EEW technique a high current density $\sim 10^{10} \text{A/m}^2$ passes through a metal in the wires-plate geometry, which leads to the formation of the metal nanoparticles. The synthesized nanoparticles are capped in de-ionized water medium, from where they are extracted by centrifugation. The synthesized nanoparticles are pure as only the pure metals are employed for their synthesis. Further, synthesized metal nanoparticles are free of any extraneous impurities as no chemicals have been used in their synthesis. Further, cost and rate of production are much better than the other techniques employed for synthesis of the metal nanoparticles. **Chapter 3** describes the characterization techniques employed to study these nanoparticles.

**Chapter 4** describes Ag nanoparticles: their synthesis employing the EEW technique, characterization by using X-ray diffraction (XRD), TEM, AFM, Zeta potential, and UV-visible spectroscopy. Fluorescence properties of the Ag nanoparticles dispersed in water have been studied in details at different excitation wavelengths. Associated with the fluorescence emission, resonant absorptions are observed in the fluorescence excitation spectra. This allows us to establish the electronic levels operating in the Ag nanoparticles. In addition, effect of solvent, concentration of Ag nanoparticles and temperature on the fluorescence of the Ag nanoparticles has been studied. In conformity with these, effect of temperature and emission wavelength has been studied on the excitation spectra. In the last section of the chapter 4, we discuss the fluorescence from trap states of the Ag nanoparticles.

**In chapter 5**, focus is on Al nanoparticles: their synthesis by employing the EEW technique and analysis using XRD, AFM, TEM, Zeta potential measurements. Also, UV-
visible spectroscopy has been employed to study the surface plasmons. Further, we discuss the fluorescence properties in details of the Al nanoparticles dispersed in water. Here, fluorescence from the Al nanoparticles has been attributed to electronic transitions from the excited states to the ground state. Also, in conformity with these, resonant absorptions in Al nanoparticles are observed, evident from the fluorescence excitation spectrum. Furthermore, effect of temperature and concentration of Al nanoparticles has been established on fluorescence of the Al nanoparticles dispersed in water.

In chapter 6, we describe briefly Fe nanoparticles and their synthesis employing the EEW technique. The Fe nanoparticles are characterized using XRD, TEM, AFM, Zeta potential measurement and UV-visible spectroscopy and their results discussed. Next, fluorescence properties of the Fe nanoparticles dispersed in water has been studied in detail. Fluorescence peaks are observed at ~303 nm at different excitation energies. In concomitant with these, resonant absorptions are observed at 224 nm and 270 nm, which allow us to give a description of the electronic levels operating in this system. Furthermore, effect of concentration of nanoparticles and temperature has been established on the fluorescence from the Fe nanoparticles.

In chapter 7, we describe the synthesis of Cu nanoparticles by employing the EEW technique. The synthesized Cu nanoparticles have been characterized by XRD, TEM, AFM, UV-visible spectroscopy and their results discussed. Surface charge of the Cu nanoparticles has been studied using Zeta potential measurements. Fluorescence peaks at ~296 nm have been observed at excitation wavelength in the range 200-240 nm and 250-280 nm. Position of the fluorescence peaks remain fixed irrespective of the excitation wavelength used. Associated with these, two resonant absorptions are observed at ~213 nm and ~269 nm, which allow us to give a description of the electronic levels operating in this system. Further, we have studied the effect of concentration of Cu nanoparticles, temperature and solvent on the fluorescence emanating from the Cu nanoparticles. We have also established fluorescence emission from the trap states of the Cu nanoparticles. Finally, the summary of the results of the present study along with conclusions has been given in chapter 8.
References